

21-4-66

German/Translation

European Patent office

European Patent Publication No. 0 122 554 B1

Date of publication: 26 March 1990

International classification: D 06 N 3/14

Application number: 84103784.9

Application date: 5 April 1984

Priority: 13 April 1983 DE 3313238

Date of publication of application:

24 October 1984, Bulletin 94/43

Date of publication of notice of grant of patent:

23 March 1990 Bulletin 90/13

Contracting states: BE DE FR GB IT NL

Reservations:

EP-A 0 089 497; DE-A 2 416 447; DE-A 3 309 424

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Title:

**APPLICATION OF POLYURETHANE PREPARATIONS CONTAINING
CROSSLINKER COMBINATIONS AS THERMOACTIVE ADHESIVE COATS**

Description

The subject of the invention is the application of 30-80 wt.% polyurethane formulations in the form of solutions, pastes or dispersion which in the solid fraction contain

I. 100 wt. pt. of relatively soft polyurethanes A) from higher-molecular polyols, 1-2.5 moles of chain lengtheners per mole of higher-molecular polyols and aliphatic and/or aromatic polyisocyanates,

II. 4-30 wt. pt. of a crosslinker combination of
B) 0.5-20 wt. pt. of formaldehyde resins and
C) 0.6-20 wt. pt. of aliphatic and/or aromatic polyisocyanates which are possibly blocked on their NCO groups and

III. the usual quantities of known additives, as thermoactivated anchor coats by the multi-coat thermoactivated reverse coating process and their thermoactivated lamination under rolling pressure at temperatures up to 160°C on textile, preferably sheetlike, substrates, especially on very light and possibly coarse-meshed fabric or knit fabric and subsequent crosslinking of the multilayered textile composite at temperatures up to 180°C.

As a result of the use of the crosslinker mixture in the PU anchor coats after their crosslinking they display surprisingly improved dry and wet adhesive values at elevated temperatures.

The production of synthetic leather for various application purposes such as outer clothing, shoe top material or as material for leather bags, purses, brief cases from polyurethane plastics by the reverse process is state of the art. Generally one practices a construction principle consisting of two or three coats, such as the top coat and anchor coat, the top coat, intermediate and anchor coat or the pre-top, top and anchor coat. The solids weight per coating generally lies between 20 and 60 g/m². As raw materials one uses solutions and dispersions of single-component as well as two-component polyurethanes as well as so called high-solid polyurethane prepolymers in block form plus polyamine crosslinkers. The 2-component polyurethanes acquire their

final plastic character only as a result of crosslinking, the high-solid prepolymers only after reaction with polyamines.

The most recent state of the art in the coating of textile sheetlike substrates is the thermoactivation process. In this process the anchor coat paste is bladed onto the top coat film which consists of several coatings such as the pre-top and top coat or the top and intermediate coat layer, the solvent (mixture) is evaporated off, the textile substrate is laminated onto the dry, thermally activated polyurethane anchor coat film on a heated cylinder under roll pressure and subsequently crosslinked at a higher temperature. The advantages of this thermoactive reversed process (also called the transfer process) for lamination include the possible low quantity of adhesive material to be applied such as 15-30 g/m² and therefore the possibility of producing lighter articles, and especially the possibility of using substrates which are not or only conditionally suitable for "wet" lamination in an organic solvent or water-containing anchor coats because of their construction or their solvent resistances, e.g., in the case of polyacrylate substrates or so called coagulates which are attacked by the solvents such as DMF under some conditions.

The disadvantages are the problems of adhesion which are observed in the articles produced by the thermoactivation transfer process. The adhesions between coating and textile substrate fluctuate in strength and especially the wet adhesion scores are relatively low. The purpose of the invention is to eliminate the above existing disadvantages of the thermoactivation process.

The subject of the invention is the use of 30-80 wt.%, especially 30-70 wt.% and usually 35-60 wt.% polyurethane formulations in the form of solutions or dispersions which, in terms of their solids content, consist of:

- I) 100 wt. pt. of relatively soft polyurethanes A), from higher-molecular polyols, with molecular weight from 600 to 6000, preferably hydroxy polyesters and/or hydroxypolyethers,
 0.1-2.5 moles, especially 0.1-1.0 mole (relative to higher molecular polyols)
 dialcohols possibly containing ionic groups and/or amino alcohols and/or
 diamines and/or hydrazine hydrate as chain lengthening agents and aliphatic or
 aromatic polyisocyanates in an NCO/XH ratio of 0.9-1.05,
- II. 4-30, preferably 5-25, especially preferably 5-22 wt. pt. of a crosslinker
 combination of
 - B) 0.5-20, preferably 1-15, especially preferably 2-12 wt. pt. of formaldehyde
 resins, preferably formaldehyde-urea and formaldehyde-melamine resins
 or polymerizates with free methylol groups or methylol groups etherified
 with lower alcohols and additionally the usual preferably acid crosslinking
 catalysts, and
 - C) 0.5-20, preferably 3-15, quite especially preferably 5-15 wt. pt. of aliphatic
 and/or aromatic polyisocyanates with at least two free or blocked NCO
 groups, where in the case of polyurethane dispersions A) only blocked,
 preferably aromatic, polyisocyanates are used, and possibly
- III) the usual quantities of other well known additives as thermoactive anchor
 coats in the multistrip thermoactive reverse coating process by blading the
 anchor coat preparations onto the separating/release paper carrying the
 top or top plus intermediate coat or a similar disposable supports, drying
 the anchor coating and its thermoactive lamination under roll pressure at
 temperatures up to 160°C with a textile substrate and subsequent

crosslinking of the composite at elevated temperature, e.g., by passing it through a tunnel at 120-180°C, preferably 120-160°C, forming crosslinked multilayered textile coatings of high adhesion.

The advantage of the process according to the invention for the production of coated articles of textile articles and polyurethanes by the multicoat reverse process, using a thermoactive polyurethane as the anchor coat consists in the mixed crosslinking of the anchor coat system with formaldehyde resins and polyisocyanates (blocked or unblocked NCO groups), in which case high dry and wet adhesive strengths are achieved in the coatings and therefore articles with high resistance to laundering and chemical dry cleaning can be produced. By the process also very light fabric/knit fabric or very open meshed fabric/knit fabrics which would "lamine through" in the case of wet coating can be laminated in very thin layers with excellent wet and dry adhesion and chemical cleaning resistance. Also very frequently small coatings of anchor coats such as 15-30 g/m² are already sufficient for thermolamination of the multilayered coating. Coatings with outstanding soft feel are obtained.

The high adhesive strengths achieved upon the crosslinking of the polyurethane formulations used according to the invention as the anchor coat from polyurethane solutions or polyurethane dispersions with addition of two types of crosslinkers from formaldehyde resins and polyisocyanates are surprising since they are not to be expected on the basis of experience acquired with the individual types of crosslinkers. The effect of the two types of crosslinkers on the adhesion of the polyurethane film to the substrates is surprisingly synergistically increased.

The relatively soft, i.e. at the thermolamination temperatures up to 150°C, preferably 90-125°C, polyurethanes consist of relatively soft, usually only moderately

high-molecular polyurethanes which achieve high quality polyurethane properties only after additional crosslinking with polyisocyanates.

They are constructed from higher-molecular polyhydroxyl compounds of the molecular weight range of 600-6000, preferably 800-4000, aromatic and/or (cyclo)aliphatic polyisocyanates and 0.1-2.5 moles of chain lengthening agents which may display also ionic groupings, preferably 0.1-1.0 moles of chain lengthener per mole of higher-molecular polyhydroxyl compound, preferably from the series of dialcohols and/or aminoalcohols, diamines and/or hydrazine hydrate and/or dihydrazide compounds. Preferably one maintains a NCO/XH ratio (XH are the groups with active hydrogen atoms reactive to isocyanates) of 0.90 to 1.05 during the synthesis or breaks and NCO excess by monofunctional chain interrupters. The reaction in this case can be performed in the melt, preferably in multishaft reaction screw machines or directly in solution. Likewise soft polyurethanes in the form of their aqueous, usually 30-70% dispersions may be used.

The reaction components for the polyurethanes A) are the well known compounds such as have been used and are frequently described in polyurethane chemistry.

The higher-molecular polyhydroxyl compounds are preferably dihydroxy polyester, polylactone, polycarbonates and polyethers or their mixtures or mixed condensates, but other higher functional polyhydroxyl compounds or polyacetals, polythioethers, polyesteramides and others may be used.

As polyisocyanates preferably one uses aromatic and/or (cyclo)aliphatic diisocyanates, e.g. the isomeric toluylene diisocyanates, diphenyl-4,4'-diisocyanate, diphenylmethane-4,4'-, -2,4'-, and/or -2,2'- diisocyanates, 3,3'-dimethyldiphenyl-4,4'-

diisocyanate, hexamethylene diisocyanate, lysine ester diisocyanate, isophoron diisocyanate, dicyclohexylmethane-4,4'-, -2,4'- and/or 2,2'- diisocyanates.

As chain lengtheners one uses especially butanediol-1,4, -1,3 and/or -2,3, ethyleneglycol, 2,2-dimethylpropanediol, hydroquinone-bis-(2-hydroxyethyl) ethers, terephthalic acid-bis-(2-hydroxyethyl) esters or also diamines such as ethylenediamine, hexanediamine, isophorondiamine, dicyclohexylmethane-4,4'-diamine also hydrazine (hydrate) or terephthalic acid dihydrazide as well as β -semicarbazido-propionic acid hydrazide and possibly also water.

As solvents for the polyurethanes one uses dimethylformamide, dimethylacetamide, N-methylpyrrolidone and other amide and/or urea-containing solvents, but preferably dimethylformamide, also tetrahydrofuran or dioxane and ketones such as methyl ethyl ketone or esters such as acetic acid ethyl ester. Preferred are mixtures of highly-polar solvents such as dimethylformamide and less polar solvents such as methyl ethyl ketone or acetic ester and possibly aromatic hydrocarbons such as toluene or xylene. In certain cases, for example, mixtures of aromatic hydrocarbons and lower molecular alcohols or ketones or cyclic ethers such as toluene and isopropanol or methyl ethyl ketone or tetrahydrofuran may be used as solvents.

The polyurethanes A) are usually fabricated from 30-80%, preferably 35-60% solutions.

As relatively soft polyurethanes A) with softening ranges below 150°C one also uses polyurethanes from dispersion. The latter are produced by known methods from the usual components: higher-molecular polyhydroxyl compounds, e.g., of the molecular weight range of 600-6000, polyisocyanates, preferably aliphatic and

cycloaliphatic diisocyanates, hydrophilizing-acting substances such as predominantly ethoxy-group-containing mono- or polyfunctional polyethers and/or compounds displaying ionic groups (preferably ionic chain lengtheners) and conventional chain lengtheners (such as dialcohols and/or amino alcohols and/or diamines or their bis-ketimines and/or hydrazine hydrate or its ketazines). The corresponding processes for their production and suitable initial components are described in the German patent documents DE AS 1 097 678, DE PS 1 184 946, DE PS 1 178 586, DE AS 1 237 306, DE OS 1 495 745, DE OS 1 595 602, DE OS 1 770 068, DE OS 1 913 271, DE OS 2 019 324, DE OS 2 811 148, DE OS 2 446 440, DE OS 2 725 589, DE OS 2 732 131 and US PS 4 192 937 and in the corresponding publications, e.g. D. Dieterich et al., Ang. Chem. 82, 53 (1970), Angew. Makromol. Chem. 76, 85 (1972) and 98, 133-165 (1981) and Progress in Organic Coatings 9, 281-340 (1981) or the literature sources cited in them.

The initial components used for the production of the polyurethane dispersion: higher molecular polyols, polyisocyanates and chain lengtheners are already known.

To incorporate hydrophilic centers for dispersability of the polyurethanes polyoxyethyl mono- or polyols are used as the only centers or mixed with ionic compounds. The ionic compounds are usually polyols containing anionic groups (e.g. SO_3^- or carboxylate or phosphoric acid groups), such as sulfonate diols per DE-OS 2 410 862 or sulfonate-group-containing polyamines (e.g. diamines modified with ethylene, propylene or butane sulfone). Cationic groups such as salts of tert-amines are suitable hydrophilic ionic centers.

Besides the ionic chain lengthening agents the usual chain lengtheners as named above are also used.

The use of soft polyurethanes A) with a softening range below 150°C as the thermoactive anchor coat in multicoat reverse coating processes also includes the use of polyurethanes with side-positioned hydroxyalkyl groups which are accessible, for example, according to DE-OS 2 732 131 in the form of dispersions.

The formaldehyde resins B) of the crosslinking mixtures II are preferably obtained from formaldehyde-urea and/or melamine resins whose methylol groups are possibly partially or totally etherified with alcohols, e.g., methanol or butanol. Melamine-methylol alkyl ethers are preferred. The resins may be solvent free, dissolved in water or dissolved in alcohols such as methanol, butanol, isobutanol or other alcohols. The concentration of these resin solutions is generally between 40 and 80 wt.%. However, methylol (ether)-group-containing copolymers may also be used such as copolymers based on methylol acrylamide.

The polyisocyanates C) of the crosslinker combination II are aliphatic and/or aromatic polyisocyanates and/or blocked aromatic polyisocyanates which display at least two NCO functions, preferably three or more NCO functions. The blocked or unblocked polyisocyanates may be used as solvent-free or as solutions. As blocking agents for the polyisocyanates ketoxines, such as methyl ethyl ketoxine, diisobutyl ketoxine, also CH-acid compounds such as malonic esters, acetoacetic ester or phenols such as phenol, nonylphenol and other blocking agents such as caprolactam come into consideration. Polyisocyanates of the type mentioned above are, among others, biuretized, possibly uretdione-containing polyisocyanates from aliphatic or cycloaliphatic diisocyanates such as hexane diisocyanate and/or isophoron diisocyanate, cyanurates from hexane diisocyanate, isophoron diisocyanate, toluylene diisocyanate-2,4/2,6 or possibly mixtures of such polyisocyanates or mixed polymerized polyisocyanates. Also

suitable are reaction products from trimethylolpropane, glycerin, pentaerythritol or other polyols in a mixture with dialcohols such as diethyleneglycol, butanediol-1,4, dipropyleneglycol and other diols with molar excess toluylene diisocyanates, diphenylmethane diisocyanates or their isomer mixtures, also reaction products from dialcohols such as di- and triethyleneglycol, di- and tripropyleneglycol with molar excessive quantities of toluylene diisocyanates or diphenyl methane diisocyanates, individually or in a mixture.

The NCO content of the polyisocyanates with NCO groups in free or blocked form is between 5 and 35%, preferably 10-20%. As blocking agents one prefers butanoneoxine, acetoacetic acid alkyl ester and/or malonic acid alkyl ester.

When polyurethane dispersions are used as A) NCO-blocked, preferably aromatic, polyisocyanates are used.

Essential for the invention is the use of a mixture of the two different crosslinker types B) and C) as a "crosslinker combination" in the polyurethanes A) of the anchor coat. In such cases the crosslinkers may be added to the polyurethanes with a mixture or as individual substances, possibly already during the preliminary steps of the polyurethane formation A). The presence and the activation of the two types of crosslinkers during the thermal crosslinking of the anchor coat is essential for the invention.

The content of formaldehyde resins is between 0.5 and 20 wt. pt.; the content of polyisocyanate C) is between 0.5 and 20 wt. pt., but the content of crosslinker combination should not exceed 30 wt. pt. so that, for example, in the case when 20 wt. pt. of B) are used, a maximum of only 10 wt. pt. of C) may be used.

Also the conventional additives can be added to the formulations in the usual quantities (usually limited to 20 wt. pt. of III) per 100 parts of A)), e.g., pigments, fillers, dyes, thickeners, flow promoters, silicones such as dimethylpolysiloxanes or ether silicones, hydrolysis, aging, oxidizing and light-protection agents, flame retardants, fungicides and similar additives.

To produce the top, pre-top and intermediate coating solutions the usual polyurethane solutions, polyurethane dispersions or polyurethane-reactive systems are used, possibly also other polymers such as PVC.

For this purpose one applies the coats to a disposable support, preferably release paper or possibly a pattern-bearing silicone matrix, solidifies them by drying at elevated temperature, usually between 90-160°C and finally applies the anchor coat of the PU preparation according to the invention, e.g. by blading, e.g., in thicknesses of 15-50 g/m², preferably 15-35 g/m² and also dries the latter, e.g., at temperature up to 100°C, especially temperatures from 60 to 85°C, in a drying tunnel pass.

The textile substrate (nonwoven, knit fabric, woven fabric, filled nonwoven, preferably a nonwoven filled with microporously-formed coagulates) is laminated under roll pressure on a preferably heated cylinder with dry thermally activated (preferably at temperatures up to 160°C, preferably 80-125°C) multilayered film on its anchor coat side and subsequently thermally crosslinked at elevated temperature, e.g. at 280°C, preferably 120-160°C. The coated material is obtained after removal of the disposable support.

In the examples the following abbreviations are used:

DMF = dimethylformamide
TOL = toluene
IPA = isopropyl alcohol

MEK = methylethyl ketone

Examples

Example 1

1.1. The PUR anchor coat preparation for the production of a two and three strip transfer coating by thermoactive lamination of the substrate is of the following composition according to the invention:

- A) 900 g of 50% PUR solution in DMF/MEK/TOL = 40/30/30, 30000 mPa·s/25°C prepared as follows:
[1000 g (0.5 mole) of ethylene glycol polyadipate, 1000 g (0.5 mole) diethylene glycol polyadipate, are reacted in the melt at 100°C with 230 g (1.32 mole) of toluylene diisocyanate-2,4/2,6 (isomer mixture 80/20) to form an NCO prepolymer; after addition of 900 g of DMF, 680 g MEK, 680 g TOL and 31.8 g of diethylene glycol (0.30 mole) the polyaddition reaction is conducted further at 80°C, and the further increase in viscosity of the solution is stopped by the addition of 2.5 g of butanoneoxime],
- B) 40 g of melamine resin (melamine hexamethylolmethyl ether), solvent free
10 g of catalyst solution composed as follows
[190 g of p-toluenesulfonic acid, 101 g N-methylmorpholine, 709 g DMF],
- C) 50 g of solution of a blocked polyisocyanate [isocyanurate from hexanediisocyanate-1,6, blocked with a mixture of malonic acid diethylester/acetoacetic acid ethylester (3:2), 75% in ethylglycol acetate/xylene (1:1), blocked NCO content ca. 10%]

1000 g

The PUR anchor coat preparation is ca. 53% [in concentration] at a viscosity of ca. 20000 mPa·s/25°C.

1.2. PUR top coat solution (not according to the invention)

900 parts (1.0 mole) of a polyester of adipic acid and butanediol (average molecular weight 900) is reacted with 87 parts (0.5 mole) of toluylene diisocyanate (65% 2,4-isomer, 35% 2,6-isomer) into a prepolymer. The OH-terminated prepolymer is reacted together with 93 parts (1.5 mole) of 1,2-ethanediol and 500 parts (2.0 mole) of 4,4'-diisocyanatodiphenylmethane in 2920 parts DMF/MEK (1:1) into a polyurethane solution. After reaching a viscosity of ca. 18000 mPa·s at 80°C the reaction is interrupted by the addition of 8 parts of butanoneoxime. One obtains a 35% solution with a viscosity of 50000 mPa·s/23°C.

1.3. Two-strip transfer coating with thermoactive anchor coat, using the PU preparation (according to the invention).

The top coat solution is pigmented with 8 wt.% (relative to 1.2) of a 40% TiO₂ pigment paste.

On a coating machine using a roller blade the pigmented top coat solution 1.2 is bladed onto a release paper (quantity applied 120 g/m²).

After the evaporation of the solvent in the first tunnel at 120-130-140°C a PUR top coat of ca. 35 g/m² is obtained on the release paper.

On the second applicator machine on the top coat sheet the thermoactive anchor coat paste 1.1, wet application 50 g/m² according to the invention, is bladed on, in the second tunnel the solid mixture is evaporated at 60-70-80°C, the dry coat weight is ca. 25 g/m². Before the third tunnel the sheet is guided over a cylinder heated at 120°C, at which time the dry anchor coat is thermally activated in order then to be laminated with

a PES fabric of 120 g/m² under a pressing pressure of ca. 4 bar. Upon passage through the third tunnel at 120-140-160°C the thermoactivated anchor coat is crosslinked during the passage through the heating tunnel (holding time about 2 minutes).

The coated article which is suitable for confectioning outer clothing, is characterized by a soft feel, a dry surface and a resemblance to nappa leather. It is essentially characterized by excellent dry and wet adhesion of the PUR to the textile.

1.4. Trials with different crosslinker quantities

The dry and wet adhesion in the case of mixed crosslinking with resin + polyisocyanate is far better than in the case of crosslinking with resin or polyisocyanate in the anchor coat preparation 1.1 alone. The values for the dry and wet adhesion (in N/2.5 m) in this case are found to be the following:

Crosslinker wt.% relative to strip paste 1.1	Dry adhesion	Wet adhesion
4.0% melamine resin 9.0% melamine resin	8-10 10-12	6-8 (ref.) 8-10 "
5.0% polyisocyanate 9.0% polyisocyanate	10-12 12-15	7-10 (ref.) 10-12 "
4.0% melamine resin 5.0% polyisocyanate	20-25	18-22 (according to invention)

Example 2

2.1a) The PUR anchor coat preparation for thermoactivated lamination of substrates is composed as follows:

- A) 900 g of 50% PUR solution in DMF/TOL/IPA = 40/35/25; 50000 mPa·s/
23°C is produced as follows:

1700 parts (1.0 mole) of a hydroxyl polyester from adipic acid and hexanediol-1,6/neopentylglycol (65/35; molecular weight 1700) is reacted with a mixture of 333 parts (1.5 mole) of isophoron diisocyanate and 84 parts (0.5 mole) of hexamethylene diisocyanate in 1605 parts of DMF/TOL (40:35), which is added in portions with increasing viscosity. For chain lengthening it is allowed to react with 45 parts (0.9 mole) of hydrazine hydrate in 535 TOL/IPA. After the 50% solution has achieved a viscosity of 18000 mPa·s at 80°C (NCO content of solution 0.1%) the reaction is terminated by stirring in 12 parts of butanoneoxime. One obtains a 50% polyurethane solution with a viscosity of 50000 mPa·s/23°C which does not change upon storage.

- B) 50 g of melamine resin solution [Maprenal MF-800, Hoechst, AG], 55% in i-butanol, 10 g catalyst solution as example 1
- C) 40 g solution of a blocked polyisocyanurate from hexane diisocyanate-1,6, blocked with butanoneoxime 75% in ethylglycol acetate, blocked NCO content ca. 10%)

1000 g

2.1b) PUR anchor coat preparation for thermoactive lamination (using two different polyurethanes)

- A/1 800 g of 50% PUR solution in DMF/TOL/IPA = 40/35/25, 50000 mPa·s/25°C as in 2.1a)
- A/2 100 g of 30% PUR solution in TOL/IPA/EG = 29:29:12, 22000 mPa·s/25°C as in 2.2
- B) 50 g melamine resin, 55% i-butanol

10 g catalyst solution as in example 1

C) 40 g blocked polyisocyanate as in 2.1a)

1000 g

The PUR anchor coat preparation is ca. 49% at a viscosity up to 30000 mPa·s/25°C.

2.2. PUR top coat solution (not per invention)

The top coat paste is a pigmented 30% solution of an aliphatic single-component polyester urethane in toluene/isopropanol/ethylglycol = 29:29:12 with a viscosity of 22000 mPa·s/25°C. The PUR is produced by reaction of a NCO prepolymer of 1700 g (1.2 mole) of polyester from hexanediol-1,6, neopentylglycol (ratio 65/35) and adipic acid and 490 g (2.2 mole) of isophoron diisocyanate with 205 g (1.2 mole) of isophoron diamine in solution.

2.3. PUR pre-top coat solution (not according to invention)

216 g (125 mole) of the polyester described under 2.2 and 76 g (0.190 mole) of a polyester of phthalic acid and ethylene glycol are mixed with 205 g (0.925 mole) of 1-isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexane (IPDI) and reacted at 80°C to a constant NCO content of 10.2%. Then the batch is allowed to cool to room temperature, diluted with 600 g toluene, another 400 g of isopropanol are added to the solution and then gradually a solution of 103 g (0.605 mole) of 1-aminomethyl-5-amino-1,3,3-trimethylcyclohexane (IPDA) and 200 g of isopropanol is then added and finally diluted once more with 200 g ethylglycol.

One obtains 2000 g of a 30% PUR solution in toluene/isopropanol/ethylglycol with a viscosity of 14000 mPa·s at 25°C.

2.4. Three coat transfer coating with thermoactive anchor coat 2.1 (according to the invention)

The unpigmented pre-top coat solution (2.3) is plated onto a release paper, wet coat weight ca. 20 g/m²; after drying (60-80-120°C) a thin pretop coat of ca. 8 g/m² is present on the release paper. On it with the pigmented paste (2.2) a top coat is bladed which has a weight of 25 g/m² after drying (70-90-120°C).

On this composite of pre-top coat and top coat using anchor coat paste 2.1a) or 2.1b) the thermoactivatable anchor coat is bladed on, wet coverage 60 g/m², dry coverage ca. 30 g/m², drying performed at 60-70-80°C. Then the sheet is guided over a cylinder heated at 125°C and by thermoactivation of the dry anchor coat is laminated with a coagulate product (nonwoven filled with microporous PU coagulate) of 200 g/m². The pressing pressure for the lamination is ca. 5 bar. Then in another passage through the channel at 120-140-160°C the thermoactivated anchor coat is crosslinked.

One obtains full, soft, voluminous articles with the corresponding feel and interesting grain pattern. The values of the dry and wet adhesion are excellent: 37 N/2.5 cm (33 N/2.5 cm) for the anchor coat 2.1a) and 40 N/2.5 cm (38 N/2.5 cm) for 2.1b).

Example 3

3.1. PUR anchor coat preparation for thermoactive lamination (according to invention)

A) 885 g PUR solution 70% in DMF, 60000 mPa·s/25°C, produced as follows:

1000 g (0.50 mole) of dihydroxypropylene-glycol polyether, 54.0 g (0.60 mole) butanediol-1,4 and 191 g (1.10 mole) toluylene diisocyanate-2,4/2,6 (isomer mixture 80/20) are reacted at 80-90°C in the melt, dissolved in

535 g DMF, and the reaction terminated with 2.0 g of N-methylethanolamine.

- B) 50 g melamine resin, solvent free
15 g catalyst solution produced from
[190 g p-toluenesulfonic acid, 149 g triethanolamine in 661 g DMF];
- C) 20 g polyisocyanate, NCO content ca. 20% (biuretized 1,6-hexane diisocyanate)
30 g polyisocyanate, NCO content ca. 20% (reaction product, 1.0 mole tripropylene glycol and 5.0 mole 4,4'-diphenylmethane diisocyanate)

1000 g

The PUR anchor coat preparation is ca. 72% in DMF, viscosity 42000 mPa·s/25°C.

3.2. PUR top coat solution (not according to invention)

2250 parts (1.0 mole) of a hydroxyl polyester from adipic acid and butanediol-1,4 (molecular weight 2250), 283 parts (4.56 mole) ethanediol and 22 parts (0.24 mole) 1,4-butanediol are reacted with 1452 parts (5.8 mole) of 4,4'-diisocyanatodiphenyl methane in 7441 parts of a mixture of DMF/MEK/TOL (60:25:15). After reaching a viscosity at 80°C of approximately 12000 mPa·s and a NCO content of a solution of 0.1% 24 parts of butanoneoxime are added and stirring is continued for ca. 1 hour at 180°C. One obtains a 35% polyurethane solution with a viscosity of 36000 mPa·s/23°C.

3.3. Two-coat transfer coating with thermoactive anchor coat 3.1 (used according to the invention)

After pigmentation with 10% of a commercial 40% color paste by the usual blading technique a top coat from the top coat solution 3.2 is produced on an

embossed release paper. Dry weight 30 g/m². By the technique described in example 1.3 the thermoactive anchor coat 3.1 is applied to the top coat (40 g/m² dry weight) and after thermoactivation at 100°C is laminated with a roughened cotton fabric of 220 g/m². Crosslinking is performed at 120-140-160-°C. The article which is suitable as shoe top material has good grain throw and outstanding adhesion to the substrate; dry: 42 N/2.5 cm, wet: 38 N/2.5 cm.

Example 4

4.1. PUR anchor coat preparation for thermoactive lamination (according to invention):

- A) 900 g PUR solution 50% DMF/TOL/IPA = 40/30/30, 20000 mPa·s/25°C
produced as follows:
[1700 g (1.0 mole) of the polyester described in 2.2 are reacted with 87.0 g (0.50 mole) of toluylene diisocyanate-2,4/2,6 (isomer mixture 80/20) in the melt at 90°C. Then the reaction is conducted further after addition of 222 g (1.0 mole) of isophorondiisocyanate at 90°C in order to obtain a NCO prepolymer. The latter is dissolved in a mixture of 840 g DMF and 625 g TOL. While stirring a solution of 12.5 g (0.25 mole) of hydrazine hydrate and 65.5 g of 4,4'-diaminodicyclohexylmethane (0.25 mole) in 625 g of IPA is added as a chain lengthener for construction of the polyurethane urea. The reaction is terminated by addition of 5 g of butanoneoxime.
- B) 40 g melamine resin, 70% in i-butanol
10 g catalyst solution as in 3.1
- C) 50 g of blocked polyisocyanate as in 1.1

1000 g

The PUR anchor coat preparation is ca. 52% with a viscosity of 12000 mPa·s at 25°C.

4.2. PUR top coat solution (not according to invention)

The top coat solution is a 25% solution of a polycarbonate-polyester urethane in DMF with a viscosity of 10000 mPa·s/25°C. The polycarbonate-polyester urethane is produced by melt condensation of 1000 g (0.5 mole) of hexanediol-polycarbonate, 1125 g (0.5 mole) of a butanediol-1,4-adipate, 270 g of butanediol-1,4 (3.0 mole) and the equivalent quantity of 4,4'-diphenylmethane diisocyanate (1000 g).

4.3. Two-coat transfer coating with thermoactive anchor coat (according to the invention)

After pigmentation with 12% of a commercial 40% TiO₂-based color paste a top coat is produced with the top coat solution 4.2 by the conventional blading technique on embossed paper of ca. 30 g/m² dry weight. Using the technique described in example 1.3 the thermoactivatable anchor coat 4.1 is bladed onto the top coat at 35 g/m² dry coating weight and laminated after thermoactivation at 120°C with an elastic knit product of polyacrylic fibers (180 g/m²). Crosslinking at 140-150-160°C. The highly elastic article for sports clothing (e.g. surfing suits) is characterized by a high adhesion to the textile substrate, dry: 40 N/2.5 cm, wet: 38 N/2.5 cm.

Example 5

5.1. PUR anchor coat preparation for thermoactive lamination (according to invention)

A/1 675 g of 50% PUR solution in MEK/TOL = 3:1, 20000 mPa·s/25°C, produced as follows:

2000 g (1.0 mole) of diethyleneglycol polyadipate are reacted in the melt with 244 g (1.40 mole) of toluylene diisocyanate-2,4/2,6 (isomer mixture 80/20) into a NCO prepolymer and after dissolving in 570 g of TOL and 17 g of MEK polyadded with 36.0 g (0.40 mole) of butanediol-1,3 at 80°C to form polyurethane. By adding 2.5 g of butanoneoxime the polyaddition reaction is stopped.

A/2 200 g of 35% PUR solution in DMF/MEK = 1:1, 40000 mPa·s/25°C, produced as follows:

800 g (1.0 mole) of hexanediol-1,6-polyadipate and 174 g (1.0 mole) of toluylene diisocyanate-2,4/2,6 (isomer mixture 65/35) are reacted in the melt into the polyester polyurethane and granulated while cooling. 350 g of granulate are dissolved in 325 g of DMF + 325 g MEK.

- B) 45 g melamine resin, solvent free
10 g catalyst solution as in 1.1
- C) 70 g polyisocyanate, 60% in butylacetate, NCO content ca. 10% [isocyanurate from hexane diisocyanate-1,6 (1.0 mole) and toluylene diisocyanate-2,4/2,6 (2.0 mole)].

1000 g

The PUR anchor coat preparation is ca. 50% with a viscosity of 23000 mPa·s at 25°C.

5.2. PUR top coat solution (not according to invention)

1000 g (0.5 mole) butanediol-1,4-polyadipate, 113 g (1.25 mole) of butanediol-1,4, 78.0 g (1.25 mole) ethyleneglycol and 750 g (3.0 mole) of 4,4'-diphenylmethane diisocyanate are polyadded in a screw reactor in the melt into

PUR and granulated while cooling. The 25% solution of PUR in DMF/TOL/MEK = 1:1:1 has a viscosity of 10000 mPa·s/25°C.

5.3. Two-coat transfer coating with thermoactive anchor coat (according to invention)

Using the technique described in Example 1.3 the thermoactivatable anchor coat 5.1 is bladed onto a top coat from 5.2 weighing 30 g/m², dried coating weight 20 g/m². After thermoactivation on the heated steel cylinder at 115°C a rayon staple product of 100 g/m² (loose fabric construction) is laminated; pressing pressure 4 bar, crosslinking 120-140-160°C. The light rayon staple article totalling 150 g/m² product weight is suitable for light outer clothing. The washing and the chemical cleaning-resistant product has good adhesion.

In another variant the anchor coat 5.1 is dried at 80-100°C, lamination is performed on the steel cylinder at 20-30°C at a pressing pressure of 6 bar; crosslinking 130-150-160°C.

Example 6

6.1 PUR anchor coat preparation for thermoactive lamination (according to invention)

A) 850 g of 50% PUR solution in MEK/TOL = 3:1, 35000 mPa·s/25°C, produced as follows:

720 g (0.90 mole) of 1,6-hexanediol polyadipate, 170 g (0.10 mole) of mixed polyadipate from 1,6-hexanediol and neopentylglycol (ratio 65/35) are reacted in a melt with 260 g (1.50 mole) of toluylene diisocyanate-2,4/2,6 (isomer mixture 80/20) into a NCO prepolymer and after dissolving in 300 g of TOL and 900 g MEK are polyadded with 45.0 g (0.50 mole) of butanediol-1,4 at 80°C to form PUR.

B) 80 g formaldehyde-urea resin, 50% in i-butanol

15 g catalyst solution as in 1.1

- C) 55 g of blocked isocyanate from tripropylene glycol (1.0 mole), 4,4'-diphenylmethane diisocyanate (5.0 mole) and butanoneoxime (8.0 mole), 50% in MEK/ethylglycol acetate = 1:1, blocked NCO content ca. 10%

1000 g

The PUR preparation is ca. 50% with a viscosity of 27000 mPa·s at 25°C.

6.2. PUR top coat solution (not according to invention)

1000 g (0.5 mole) of butanediol-1,4-polyadipate, 300 g (1.35 mole) of isophoron diisocyanate are reacted in a screw reactor in the melt into the prepolymer. The polyurethane urea is formed after 222 g (0.85 mole) of 4,4'-diamino-dicyclohexylmethane are fed into the melt; this is followed by extrusion, cooling, and granulating. The 25% solution of the granulate in toluene/isopropanol/ethylglycol has a viscosity of 12000 mPa·s/25°C.

6.3. Two-coat transfer coating with thermoactive anchor coat (according to invention)

The thermoactive anchor coat 6.1 is bladed onto a top coat weighing 25 g/m² from 6.2 using the technique described in example 1.3. Dry weight 25 g/m². After thermoactivation on the heated steel cylinder at 120°C a wide meshed polyamide knit product with a product weight of 100 g/m² is laminated. Pressing pressure 4 bar, crosslinking 120-140-160°C. The light elastic article is suitable for outer clothing. With good laundry and the chemical cleaning-resistance the product has good adhesion.

Example 7

7.1a) PUR anchor coat preparation for thermoactive lamination (according to invention)

- A) 930 g of 40% anionic PUR dispersion in water

1721 g of diethyleneglycol adipate (molecular weight 2500), 213 g 1,2-propyleneglycol polyether (molecular weight 1000), 107 g polyether from 85% ethylene oxide and 15% propylene oxide, started on n-butanol (molecular weight 1250), 205 g propoxylated adduct from butenediol-1,4 and sodium bisulfite (molecular weight 425) are reacted after dehydration in the vacuum at 100°C with 390 g of toluylene diisocyanate-2,4/2,6 (isomer mixture 65/35) in the melt into the NCO prepolymer at 100°C. The reaction is continued until a NCO content of 3.0% is reached. The melt is cooled to 50°C and while stirred mixed with 67.0 g of acetone. With vigorous stirring 4050 g of water (deionized) are allowed to flow in. The anionic dispersion thus obtained is then stirred for five hours at 70°C and then cooled to room temperature. The dispersion has a solids content of 40%.

- B) 15 g melamine resin, 50% in water
10 g catalyst solution
- C) 45 g of blocked polyisocyanate (isocyanurate as in 1.1)

1000 g

The ca. 42% PUR anchor coat preparation is mixed with 1.5% of a polyacrylic acid solution in order to adjust the application viscosity, the pH is adjusted with concentrated ammonia to 8-9; viscosity ca. 6000 mPa·s/25°C.

7.1b) PUR anchor coat preparation for thermoactive lamination (according to invention)

- A) 800 g of a 40% PUR dispersion in water according to 7.1a)
125 g of 50% aliphatic PUR dispersion

1700 g (1.0 mole) of a mixed polyester of hexanediol-1,6, neopentylglycol and adipic acid are reacted with 303 g (1.8 mole) of hexane-1,6-diisocyanate into an NCO prepolymer; the latter is constructed in aqueous dispersion with 152 g (0.8 mole) of ethylenediamine ethylsulfonic acid sodium as chain lengthener into the polyester urethane urea, solids content 50%.

- B) 15 g melamine resin solution (Cassurit HML, Hoechst AG), 50% in water
10 g catalyst solution as in example 1
- C) 50 g of blocked polyisocyanate as in 1.1, NCO content ca. 10%

1000 g

The ca. 43% PUR anchor coat preparation is mixed with 1.0% of a 10% polyacrylic acid solution in order to adjust the application viscosity, the pH is adjusted to 8-9 with concentrated ammonia; viscosity ca. 8000 mPa·s at 25°C.

7.1c) PUR anchor coat preparation for thermoactive lamination (according to invention). 800 g of 40% PUR dispersion in water produced as follows: 2638 g of the NCO prepolymer produced in the melt under 7.1a), NCO content 3.0%, is mixed after cooling to 50°C with 67.0 g of acetone and 335 g of blocked isocyanate (produced according to 1.1). 4440 g of deionized water are stirred into the mixture. The dispersion thus obtained is then stirred at 70°C for 5 hours and then cooled to room temperature; solids content 40%.

175 g polyacrylate dispersion, 40% in water (mixed polymerizate from 300 g acrylic acid butyl ester, 80 g styrene and 20 g of N-methylol acrylamide in 600 g water)

15 g melamine resin, 50% in water

10 g catalyst solution as in 1.1

1000 g

The ca. 40% anchor coat preparation is thickened with a 1.5% of a 10% polyacrylic acid solution in water in order to adjust the application viscosity. Viscosity ca. 6000 mPa·s/25°C.

7.2. PUR top coat of dispersion (not according to invention)

545 g of PUR dispersion, 50% as described in 7.1b)

455 g of PUR dispersion, 40% produced from

485 g hexanediol-1,6-polyadipate (OH number 134)

20 g trimethylolpropane

85 g propoxylated adduct from 2-butenediol-1,4 and NaHSO₃ (molecular weight 425)

365 g of 4,4'-dicyclohexylmethane diisocyanate

67 g 1,6-hexane diisocyanate

50 g acetone

107 g N-methylpyrrolidone

1500 g desalinated water

Execution: cf. DE-A 2 811 148

1000 parts of PUR top coat dispersion, ca. 45%, are stirred with 15 parts of polyacrylic acid thickener and 100 parts of an aqueous pigment preparation. After adjustment of the pH to 8-9 concentrated ammonia the coating paste has a viscosity of ca. 10000 mPa·s at 25°C.

7.3. Two coat transfer coating with thermoactive anchor coat (according to the invention)

Using the technique described in example 1.3 the thermoactive anchor coat paste 7.1a), 7.1b) or 7.1c) were bladed onto a 28 g/m² top coat produced from the dispersion coating paste 7.2, dry coating weight 22-25 g/m². After thermoactivation on a steel cylinder heated to 115°C a cotton/polyester fabric of 120 g/m² is laminated on at 4 bar pressing pressure, crosslinking at 120-140-160°C. The PUR coating produced from the dispersion adheres very well to the textile, which assures excellent laundry and dry cleaning resistance.

Example 8

8.1. PUR anchor coat preparation for thermoactive lamination (according to invention)

A/1 750 g of 50% PUR solution in DMF/TOL/MEK = 55/25/20, 25000 mPa·s/25°C produced as follows:

2500 g (1.0 mole) of diethylene glycol-polyadipate are reacted in the melt at 100°C with 230 g (1.32 mole) of toluylene diisocyanate-2,4/2,6 (isomer mixture 65/35) into a NCO prepolymer. To this one adds 1520 g of DMF, 690 g TOL and a solution of 13.5 g (0.15 mole) of butanediol-1,4 and 17.7 g (0.15 mole) of hexanediol-1,6 in 550 g MEK and conducts the polyaddition further at 80°C. The NCO reaction is terminated by addition of 2.0 g of butanoneoxime.

A/2 160 g of 40% PUR solution in DMF, 46000 mPa·s/25°C

2250 parts (1.0 mole) of butanediol-1,4-polyadipate and 216 parts (2.4 mole) of 1,4-butanediol are reacted with 851 parts (3.4 mole) of 4,4'-diisocyanate diphenylmethane into a polyurethane solution in 4976 parts DMF/toluene (3:2). At 80°C one reaches an approximate viscosity of 17000 mPa·s, and the polyaddition reaction is terminated with 50 parts of

butanoneoxime. A 40% solution with a viscosity of 46000 mPa·s/23°C is obtained.

B) 35 g melamine resin, solvent-free

10 g catalyst solution as in 1.1

C) 45 g blocked aromatic polyisocyanate as in 6.1

1000 g

The PUR preparation is ca. 50% and has a viscosity of 28000 mPa·s at 25°C.

8.2. PUR top coat solution as in 1.2

8.3. Two-coat transfer coating with thermoactive anchor coat (according to the invention)

Using the technique described in example 1.3 the thermoactive anchor coat from the paste 8.1 is bladed onto a 30 g/m² top coat produced from the coating paste according to example 1.2, dry coating weight ca. 30 g/m². After thermoactivation at 80°C a bound nonwoven of 200 g/m² product weight is laminated. Crosslinking 130-150-160°C. The article which can be used for making leather goods is characterized by outstanding adhesion of the PUR to the substrate.

Example 9

9.1. PUR anchor coat preparation for thermoactive lamination

A/1 800 g of 50% PUR solution in DMF/TOL/IPA = 50:25:25, 30000 mPa·s/25°C produced as follows:

2000 g (1.0 mole) of dihydroxypropyleneglycol polyether are reacted with 278 g (1.60 mole) of toluylene diisocyanate-2,4/2,6 (isomer mixture 80/20) at 100°C in the melt into the NCO prepolymer. After the prepolymer is dissolved in 1174 g of DMF and 387 g of TOL a solution of 35.5 g (0.40

mole) of N-methyl propanolamine-1,2 in 200 g of TOL are allowed to flow in at 80°C. After 30 minutes of reaction at this temperature one adds at 40°C a solution of 34.0 g (0.20 mole) of isophoron diamine in 587 g of IPA. Finally the polyaddition is terminated by addition of 3 g of diisobutylketoxime.

A/2 100 g of 40% PUR solution in DMF/TOL/MEK = 37:35:28, 30000 mPa·s/25°C produced as follows:

A solution of 2000 parts (1.0 mole) of a linear propylene oxide-polyether started with 1,2-propanediol (molecular weight 2000) in 660 parts of DMF is reacted with 676 parts (2.7 mole) of 4,4'-diisocyanatodiphenyl methane.

The prepolymer obtained is allowed to react with 150 parts (0.05 mole) of a trifunctional propylene oxide polyether started with trimethylol propane and with an average molecular weight of 3000 and with 153 parts (1.7 mole) of 1,4-butanediol.

During the reaction one dilutes in portions with 1000 parts of DMF, 1580 parts of toluene and 1260 parts MEK to form a 40% solution. With another 25 parts of 4,4'-diisocyanatodiphenyl methane the desired viscosity is reached, and the reaction is terminated by addition of 15 parts of butanoneoxime. One obtains a viscosity-stable solution of 30000 mPa·s/23°C.

B) 40 g melamine resin, 70% in i-butanol

10 g catalyst solution as in 3.1

C) 50 g of blocked polyisocyanate as in 1.1

1000 g

The PUR preparation is ca. 51% [in concentration], the viscosity is 28000 mPa·s/ 25°C.

9.2. PUR top coat solution (not according to invention)

2000 g (1.0 mole) of dihydroxy-oxytetramethylene polyether are reacted with 490 g (2.20 mole) of isophoron diisocyanate in the melt at 100°C into the NCO prepolymer. The latter is dissolved in 2800 g of TOL. At 20-25°C to it a solution of 315 g (1.20 mole) of 4,4'-diaminodicyclohexylmethane is 2800 g of IPA and 900 g of ethylglycol are allowed to flow in. The polyaddition reaction is stopped by adding 1.0 g of diisobutylamine.

Viscosity of the 30% solution: 32000 mPa·s/25°C.

9.3. Two strip transfer coating with thermoactive anchor coat (according to invention)

Solution 9.2 is mixed after pigmenting with 10% of a commercial pigment paste with 0.4%, relative to the PUR solid, of a light-protection agent based on tetramethylpiperidine (Tinuvin 292/Ciba Geigy, Basel, Switzerland). Using the technique described in Example 1.3 the thermoactive anchor coat 9.1 is bladed onto a 30 g/m²-weighing top coat from said coating paste, dry coating weight ca. 30 g/m². After thermoactivation at 120°C a roughened cotton product, 240 g/m² is laminated, pressing pressure 4 bar, cross linking at 130-150-160°C. The extremely hydrolysis-resistant articles can be used as upholstery material. The adhesion of the PUR layer to the textile is excellent.

Example 10

10.1. PUR anchor coat preparation for thermoactive lamination (according to invention)

- A1) 700 g of 30% PUR solution in DMF/ethylacetate = 20:80, 35000 mPa·s/25°C produced as follows:
- 1000 g (0.50 mole) ethyleneglycol adipate, 1000 g (0.50 mole) diethylene glycol adipate are reacted in the melt with 174.0 g (1.0 mole) of toluylene diisocyanate-2,4/2,6 (isomer mixture 80:20) into the polyester polyurethane and granulated while cooled, 300 g of granulate are dissolved in 140 g of DMF and 560 g of ethylacetate.
- A/2 200 g of 98% PUR paste in ethylacetate, 22000 mPa·s/25°C produced as follows
- 1000 g of adipic acid polyester from diethylene glycol and trimethylol propane (OH number 28) are reacted with 80 g of a polyisocyanate, NCO content 13%, 75% in ethylacetate at 70°C. The polyisocyanate is obtained by reacting trimethylol propane, butanediol-1,3 with toluylene diisocyanate.
- B) 25 g melamine resin, solvent free
- 5 g catalyst solution as in 1.1
- C) 70 g of 75% polyisocyanate from trimethylolpropane, butanediol-1,3 in TDI) in ethyl acetate, NCO content 13% (see above, production described under A/2)

1000 g

The PUR anchor coat formulation is ca. 48% in concentration. Viscosity 28000 mPa·s/25°C.

10.2. PUR top coat solution as in 5.2

10.3. Two-coat transfer coating with thermoactive anchor coat (used according to invention)

On a top coat weighing 30 g/m² from the top coat paste in 5.2 using the technique described in example 1.3 the thermoactive anchor coat 10.1 was bladed on; dry weight 22 g/m², drying performed in the coating channel at 20-30°C. After thermoactivation in the hot cylinder (125°C) a cell wool fabric of less than 100 g/m² is laminated at 5 bar pressure. Cross linking at 100-120-150°C. The product is resistant to laundering and chemical cleaning.

Claims

1. The use of 30 to 80% strength polyurethane formulations in the form of solutions or dispersions, whose solids content comprises

I. 100 parts by weight of relatively soft polyurethanes

A) made from high molecular weight polyole, 0.1 to 2.5 mole of chain extenders per mole of high molecular weight polyols and aliphatic and/or aromatic polyisocyanates,

II. 4 to 30 parts by weight of a crosslinking agent a combination composed of

B) 0.5 to 20 parts by weight of formaldehyde resins and

C) 0.5 to 20 parts by weight of aliphatic and/or aromatic polyisocyanates,

which may if desired be blocked at their NCO groups, the sum making up 4-30 parts by weight and

III. Customary amounts of additives known per se, as heat activatable anchor coatings in multilayer heat sensitive reverse roll coating processes, and heat activated lamination of the said anchor coatings under roll pressure at temperatures up to 160°C with textile backings and subsequent crosslinking of the multilayer/textile composite at temperatures up to 180°C.

2. The use of formulations according to Claim 1, characterized in that the solid material of the polyurethanes A) is formed from high molecular weight polyols having molecular weights from 600 to 6000, 0.1 to 2.5 mole, per mole of high molecular weight polyols, of dialcohols, aminoalcohols, diamines, each of which may if desired contain ionic groups, and/or hydrazine hydrate as chain extenders and aliphatic or aromatic polyisocyanates.

3. The use of formulations according to Claims 1 and 2 characterized in that they comprise 5 to 25 parts by weight of a crosslinking agent combination II) made from

B) 1 to 15 parts by weight of formaldehyde resins and acidic crosslinking catalysts thereof and

C) 3 to 15 parts by weight of aliphatic and/or aromatic polyisocyanates which if desired may be blocked at their NCO groups, the sum making up 5 to 25 parts by weight.

4. The use of formulations according to Claims 1 to 3 characterized in that they comprise 30 to 70% strength solutions having a solids content composed of

I. 100 parts by weight of relatively soft polyurethanes

A) having a softening range below 150°C, made from high molecular weight polyols of molecular weight 600 to 6000, 0.1 to 1.0 mole, per mole of high molecular weight polyol, of dialcohols, aminoalcohols; diamines and/or hydrazine hydrate and aliphatic and/or aromatic polyisocyanates.

II. 5 to 25 parts by weight of a crosslinking agent combination made from

B) 1 to 15 parts by weight of melamine-formaldehyde resins and acidic crosslinking catalysts thereof and

C) 3 to 15 parts by weight of aliphatic and/or aromatic polyisocyanates which may if desired be blocked at their NCO groups with butanone oxime, alkyl acetoacetates and/or alkyl malonates, the sum making up 5 to 25 parts by weight, and

III. Customary amounts of additives known per se.

5. The use of formulations according to Claims 1-3 characterized in that they comprise 30 to 70% strength aqueous dispersions having a solids content composed of

I. 100 parts by weight of relatively soft polyurethanes

A) having a softening range below 150°C made from high molecular weight polyols with molecular weights from 600 to 6000, 0.1 to 2.5 mole, per mole of high molecular weight polyols of dialcohols, aminoalcohols, diamines, each of which may if desired contain ionic groups, and/or hydrazine hydrate as chain extenders and aliphatic or aromatic polyisocyanates,

II. 5-25 parts by weight of a crosslinking agent combination made from

B) 1 to 15 parts by weight of melamine formaldehyde resins and acidic crosslinking catalysts thereof and

C) 3 to 15 parts by weight of aromatic polyisocyanates which have been blocked at their NCO groups, the sum making up 5 to 25 parts by weight and

III. Customary amounts of additives known per se.

6. The use according to Claims 1 to 5 of the polyurethane formulations by knife application to release papers carrying top coatings or top coatings plus intermediate coatings or to similar temporary backings, drying the anchor coating at temperatures up to 100°C, laminating the textile substrate under roll pressure on drums heated to 160°C and subsequently crosslinking at elevated temperatures up to 180°C and removing the temporary backing.

